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CONSORTIUM FOR COMMERCIAL CRYSTAL GROWTH

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INTRODUCTION

The Consortium began in 1986 as a Center for the Commercial Development of Space, funded by NASA's Office of Commercial Programs (since merged into other organizations at NASA Headquarters). The original name, Center for the Development of Commercial Crystal Growth in Space, reflected our dream of growing crystals commercially in space. After the Challenger explosion, we came to realize that we were more likely to contribute to advances in commercial crystal growth on earth. Thus we took our present name in 1992. The following mission statement and goals were established at that time.

CONSORTIUM MISSION STATEMENT

To enhance the global competitiveness of American industry by improving crystal products and processing, through space and ground-based research and development.

CONSORTIUM GOALS

1. Make significant technological advances
2. Become self sufficient
3. Provide benefits to industry
4. Provide rewards for participants
5. Exploit value of research in space
6. Commercialize crystal growth and thermal processing in space
7. Educate future scientists and engineers
8. Become a world recognized consortium in crystal products and processing

The research and development aimed at fulfilling the Consortium's mission emphasized improvements in the growth of bulk crystals for infrared sensors, radiation detectors, electronic devices, photonic and optical systems. Materials investigated included cadmium telluride and related alloys, gallium arsenide, indium antimonide, germanium cadmium arsenide, bismuth germanate and silicate, mercury halides, triglycine sulfate, and l-arginine phosphate. Several major growth techniques were improved, with applications to many other materials of commercial importance.

The Consortium's activities also included film growth and device structures, especially in the Robotic Thermal Processing project. Investigated were mercury cadmium telluride films for night vision, indium arsenide Hall generators, zinc sulfide electroluminescent flat panel displays, III-V superlattices for optoelectronic devices, silicon-germanium alloys for high speed transistors and light emitting diodes, and photovoltaic materials.

The Consortium also collaborated with the Battelle CCDS on zeolite crystallization. Zeolites are used extensively as catalysts in the petrochemical industry, and have potential applications for radiation waste concentration and bioprocessing separations.

The approach consisted of a combination of ground-based research, theoretical modelling, and flight experiments. The work was carried out in collaboration with small businesses and large, other CCDS's, NASA field centers, other government laboratories, state governments, the Canadian Space Agency, and professional societies.

Below are listed the organizations that participated in Consortium activities, including the primary subcontractors, those that contributed money, and those that donated value-in-kind (services, supplies, or equipment). We also show organizations with which we collaborated.

Primary subcontractors:
- Alabama A&M University
- Clarkson University
- University of Florida
- National Institute of Standards & Tech
- Rensselaer Polytechnic Institute
- Rockwell
- Worcester Polytechnic Institute

Cash contributors:
- EDO Barnes Engineering
- Boeing
- Grumman
- National Aeronautics and Space Administration
- The New York State Center for Advanced Materials Processing
- Rockwell
- Teledyne-Brown Engineering
- Westinghouse

Value-in-kind contributors:
- EDO Barnes Engineering
- Advanced Ceramics
- Astropower
- Brimrose
- Casting Analysis
- Florida State Space Authority
- F.W. Bell
- GFI Advanced Technologies
- Hughes
- Johnson-Matthey
- Kopin
- Macrodyne
- MetroLaser
- Potsdam Semiconductors
- Photon Energy

	Quantum Technologies Rockwell Spire Texas Instruments Two Six Westinghouse
Collaborators:	CCDS at U. Alabama, Huntsville CCDS at Battelle CCDS at U. Michigan Brookhaven National Laboratory Canadian Space Agency CANMET Dalhousie University George Mason University NASA Goddard

This report is organized by the growth techniques on which research and development were concentrated. Summaries are given in the body of the report, with details in the appendices.

VAPOR TRANSPORT

In vapor transport crystal growth, a solid feed material is placed at the hot end of a sealed ampoule. This material evaporates and is transported to the cold end of the ampoule where it condenses out, hopefully, as a single crystal. Gravity influences the transport of the growth material because of buoyancy-driven convection in the gas phase. The vapor growth of cadmium telluride and mercury halides were investigated at Rensselaer Polytechnic Institute by Professors Wiedemeier, Glicksman and Jones. Their reports are given in the appendix.

Cadmium telluride

The primary commercial objective of this project was improved infrared detectors, especially infrared focal plane arrays fabricated from mercury cadmium telluride films on cadmium telluride substrates. Such arrays are produced commercially and would benefit greatly from improved substrates and films. Infrared detectors find applications in many systems, including spectrometers, night vision goggles, medical imaging, and detection of thermal leaks in structures. Other current commercial applications for CdTe are nuclear particle detectors and photovoltaic cells. There are a wide variety of other potential commercial applications that await improved material to be realized, including laser windows, non-linear optical devices, and refracto-optic devices. Harmful defects include precipitates, grain boundaries, twin boundaries, dislocations, impurities and compositional variations.

The Consortium project on vapor growth of CdTe began in late 1986 as one of the founding projects. However, in a sense it began much earlier. The principal investigator, Professor Wiedemeier at RPI, was the pioneer on vapor transport crystal growth in space. He had experiments in Skylab, Apollo-Soyuz, STS-7 and D-1 missions. These experiments demonstrated that more perfect crystals grow in space by this technique. Recently with MSAD funding he grew films of HgCdTe in USML-1. These films were much smoother than those formed on earth.

This project was of particular interest to many companies affiliated with the Consortium: Texas Instruments, Grumman, Rockwell, Brimrose, Two-Six, and Potsdam Semiconductors.

Professor Wiedemeier was very successful in his ground-based research. As described in the Appendix, he learned how to purify CdTe and Zn-doped CdTe, seed the growth in a desired orientation, grow at a rate approaching that used commercially for melt growth, and grow diameters of commercial interest. Current commercial practice utilizes directional solidification from the melt. Vapor growth is accomplished at a much lower temperature. The advantage of a lower temperature growth is that the purity of the crystal is higher, the temperature gradients during growth tend to be smaller, the crystal is stronger so that it is degraded less by thermal stress, the composition range of the compound is narrower so that the driving force for precipitation is reduced, etc. Before Professor Wiedemeier's breakthroughs, vapor growth was too slow and the diameters too small for commercial practice.

In ground-based experiments the growth rate was increased to 40 mm/day. This is the highest growth rate ever achieved for vapor growth of CdTe, and is comparable to that used commercially for melt growth. The diameter of the bulk crystals was increased to 20 mm, which is large enough to be of commercial interest. Dislocation densities and twinning were relatively low. Precipitates were not observed.

Flight experiments were necessary to determine the improvement of CdTe caused by vapor growth in space. The value added by growth in space had to be determined in order to know what launch costs would be required for commercial growth in space. Boeing had intended to incorporate CdTe ampoules from the Consortium in its October 1992 flight of its CVTE, but we were unable to meet Boeing's delivery schedule. Boeing constructed CVTE with its own funds and flew CdTe vapor transport experiments in 1992 under a JEA.

On Spacehab-2 in 1993 we processed a CdTe vapor transport ampoule in SEF, the UAH CCDS's model of CVTE. The Consortium assisted the UAH CCDS with debugging the SEF. In comparison to identical experiments performed on earth in the SEF under otherwise identical conditions, much less spurious nucleation occurred in space and the resulting material had much larger single crystal grains with fewer twins.

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Mercurous chloride

Closely connected to Professor Wiedemeier's research was another Consortium project at RPI, under the direction of Professors Martin Glicksman and Owen Jones. The object was to view the convection in a mercury halide vapor transport crystal growth cell, in order to improve the quality of the resulting crystals through optimization of the growth cell, the furnace, and the growth conditions. This was accomplished in collaboration with Westinghouse's Research and Technology Center. (Westinghouse grows mercurous chloride crystals and uses them to fabricate radiation detectors.) Hardware was developed for measurement of extraordinarily low velocities using laser doppler velocimetry. This technology was transferred to a small business, Macrodyne. An improved growth cell was invented and Westinghouse applied for a patent (see below).

Ground-based experiments showed that instabilities in buoyancy-induced convection can induce defects in the crystal during growth.

Details are given in the Appendix. Our new low-velocity laser doppler velocimeter guided the characterization of the convection and the development of the new and improved growth furnace.

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DIRECTIONAL SOLIDIFICATION

The primary goal of this project was improved devices for infrared sensors, detectors, optical systems, and electronics. Emphasis was on directional solidification of CdTe, the applications for which were given above. However the techniques developed are applicable to a wide variety of materials of technological and commercial importance.

Research on directional solidification of CdTe began at Clarkson University in late 1986 as one of the founding projects in the Consortium. Development of the Commercial Crystal Growth Furnace began about 1990, initially under the direction of Professor Frederick Carlson. However in a sense this project began long before the Consortium. Professor Wilcox had been doing research on directional solidification for 30 years, and had an experiment on Skylab. Professor Carlson was a pioneer in modelling of directional solidification; his experience led to his proposal to develop the CCGF.

In 1991 we were joined by Professor Liya Regel, who took over responsibility for the Consortium's experimental program and became Associate Director of the Consortium. Professor Regel headed the effort on materials processing in space at the USSR Space Research Institute in Moscow. She had participated in approximately 150 flight experiments on materials processing, far more than any other scientist. She also pioneered directional solidification in the centrifuge, and showed that superior crystals can sometimes be produced this way.

Some companies interested in the directional solidification work at Clarkson included Grumman, Rockwell, Two-Six, Texas Instruments, Johnson Matthey, Advanced Ceramics, and Potsdam Semiconductors. Dr. David Larson at Grumman collaborated with us in a highly successful experiment on USML-1 with directional solidification of Zn-doped CdTe in the TBE CGF. Reflight was approved for USML-2. Grumman also had a ground-based CdTe growth program, in which it has invested several million dollars of company funds. Modelling results by Professors Carlson and John Moosbrugger showed remarkable agreement with Grumman's experimental results. Although Grumman did not plan to sell CdTe commercially, it does utilize CdTe focal plane arrays for its systems. Grumman transfers technology to its suppliers so that its systems will perform better than those of their competition.

The original concept for flight experiments on CdTe solidification was to take advantage of the reduced contact with the ampoule so often observed from directional solidification in space, starting with Skylab results in the mid 1970's. (Over a portion of their length, crystals often grew without contacting the ampoule wall.) We hypothesized that use of non-wetting coatings could make this phenomenon reproducible. We also predicted that such detached solidification would yield crystals vastly superior to those grown on earth. The USML-1 experiment seemed to verify this prediction. A portion of the ingot grew without contacting this ampoule. No new twins were generated in this region. Since twins are a serious problem in CdTe and many other semiconductor materials, this is a highly significant observation.

The above non-contacting phenomenon remained a mystery until 1993, when we were able to explain it. We now understand why it occurs and how to accomplish it reproducibly. A non-wetting and non-sticking ampoule surface is required, as well as the absence of global convection in the melt.

Technology developed in this project is being applied by Two-Six Corporation for the commercial growth of CdTe by the Bridgman technique. They modified their annealing procedure to greatly reduce precipitate size and density. Former doctoral students were employed by II-VI, Johnson-Matthey, and Texas Instruments.

The Consortium demonstrated a major advance in directional solidification growth technology. A doctoral student, Rajaram Shetty, developed a technique for coating the interior of growth ampoules with a thin, transparent film of pyrolytic boron nitride. He demonstrated that this film reduces sticking of the ingot to the ampoule and thereby dramatically reduces the dislocation density in the resulting crystals. Ampoules were coated for Grumman and Johnson-Matthey to evaluate this coating for CdTe growth. We believe our pyrolytic boron nitride coating has advantages for growth of many other crystals, not only CdTe, by the Bridgman technique.

Development of the Commercial Crystal Growth Furnace was initiated in 1991 without Consortium funding utilizing an MS student, Mr. Todd Stevens. The first prototype met design parameters. The second prototype was tested on the large centrifuge that was constructed at Clarkson by a doctoral student, Mr. Ramnath Derebail.

Another Consortium activity of increasing interest to industry was materials processing at high gravity. In 1993 we completed and put into operation our unique centrifuge facility, the first of its kind to be devoted to materials processing research and related flow visualization. The second CCGF prototype was used on this centrifuge by Mr. Derebail to grow InSb crystals. A visiting professor, Dr. Luiz Ladeira, grew Zn-doped CdTe on it at different g levels. Centrifugation made the Zn concentration slightly more uniform, did not influence the microstructure or dislocation density, and caused a marked decrease in the density of precipitates. A doctoral student, Dr. William Arnold, collaborated with Dr. Arnon Chait at NASA Lewis to use theoretical modelling to explain how solidification in a centrifuge can lead to homogeneous crystals. In 1993 we also hosted the Second International Workshop on Materials Processing at High Gravity, with attendees from around the world.

Because of Consortium research results, the CdTe growth industry is currently paying a great deal of attention to the eddy current technique. In this technique one can monitor the resistivity field throughout the melt and the ingot during solidification. With cost sharing and collaboration with a Consortium affiliate, Casting Analysis, doctoral student Gary Rosen made some exciting observations about CdTe solidification. Reflux of condensing Cd was observed on the top of the ampoule during growth. The melt tended to stratify, probably as a consequence of this refluxing. A rapid resistivity change was observed as the ingot cooled, possibly the first *in-situ* observation of precipitate formation in CdTe. Graduate student Jeff Thompson is continuing this work with funding from the NASA Graduate Student Research Program. Two-Six and other companies are investigating the use of the eddy current technique to improve and control their growth processes.

Other consortium results at Clarkson University included the following:

1. Doctoral student Jianjun Shen showed that twinning in CdTe is not caused by mechanical deformation alone.

2. Mr. Shen determined the influence of annealing conditions on properties and defects in CdTe.

3. MS student John Rydzewski and post-doc Dr. Cai elucidated the mechanism for the influence of gravity-driven convection on the microstructure of fibrous eutectics.

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SOLUTION CRYSTAL GROWTH

The primary goal of this project was to produce crystals yielding superior room temperature infrared detectors and second harmonic generation optical devices. Emphasis was on growth of doped triglycine sulfate (TGS) and L-arginine phosphate (LAP) crystals from aqueous solutions. NSF also funded work on solution growth of organic compounds --- 3-methoxy-4-hydroxy-benzaldehyde (MHBA) and mixtures of methyl-(2,4-dinitrophenyl)-aminopropanoate (MAP) and 2-methyl-4-nitroaniline (MNA) --- for second harmonic devices.

TGS infrared detectors operate at room temperature and have a wide range of commercial applications, including military systems, monitors for environmental analysis, astronomical telescopes, observation cameras as vidicon targets, and Fourier transform infrared spectrometers. LAP, MHBA and MAP-MNA second harmonic generation devices have potential commercial applications to photonic systems and for use in conjunction with high power lasers for applications such as inertial confinement nuclear fusion.

Professor Ravindra Lal's Consortium work on doped TGS was initiated at Alabama A&M University in late 1986 as one of the founding projects. Professor Lal had begun work on solution growth of undoped TGS in 1977, with funding from NASA's MSAD. Work on LAP for the Consortium began about one year later upon the recommendation of our industrial members, especially Westinghouse. The solution growth of MHBA and MAP-MNA was started in 1993.

With funding from MSAD, Professor Lal flew his first set of experiments on Spacelab 3 in 1985. His second experiment was performed in 1992 on IML-1. Both flight experiments yielded crystals superior to those grown on earth, and superior infrared detectors. No boundary could be seen between seed and grown layer; this had not been observed in earth-grown crystals. This boundary is caused by trapped solution in the form of inclusions, which generate dislocations and reduce the quality of the entire crystal. We believe the absence of inclusions in space-grown crystals is because the transition between dissolution and growth is very gradual, due to the great reduction in buoyancy-driven convection.

These results suggest that solvent inclusions can be avoided on earth if great improvements in temperature control and programming are made.

This project was supported by Teledyne Brown, EDO/Barnes Engineering, Hughes Aircraft, MetroLaser, and Quantum Technologies. Hughes Electro-optic Division donated $45,000 for growth of non-linear optical crystals, and collaborated with Professor Lal. Teledyne Brown duplicated for company use the LAP growth setup and techniques, and assisted with the conceptual design of the Commercial Solution Crystal Growth Facility flight hardware (construction of which was not begun due to termination of the CCDS). Barnes fabricated IR detectors from the TGS crystals grown at AAMU and in space. MetroLaser also assisted with the conceptual design of the CSCGF flight apparatus. Quantum Technologies was a small commercial crystal growth company that concentrated on growth from aqueous solutions; it provided advice on commercial practice and TGS seed crystals. Collaborators included:

Dr. Grant Albright, EDO/Barnes Engineering Company.

Dr. James D. Trolinger, MetroLaser.

Dr. Robert W. Byren, Hughes Electro-optic Division

Mr. Gary M. Arnett, CVC Associates

Dr. Steve Velsko, Lawrence Livermore National Laboratory

Dr. Sukant Tripathi, Lowell University

Dr. Robert Metzger, University of Alabama at Tuscaloosa

Dr. B. Loo, University of Alabama at Huntsville

Drs. B. Penn and Don Frazier, NASA Marshall Space Flight Ctr.

Ground-based research produced the following results:

1. A modified solution growth system was developed for growth of organic crystals. The temperature of the solution was programmed down while the seed crystal was rotated and pulled from the solution. Optical quality crystals of MAP-MNA and MHBA were grown.

2. Large crystals (80x80x20 mm^3) of deuterated LAP were grown by mounting the seed crystal along the b-axis.

3. Simultaneous addition of inorganic and organic dopants to TGS yielded a higher figure of merit and detectivity (D*) for infrared detectors than achieved before.

4. Doping TGS with urea increased the normalized growth yield, improved the pyroelectric constant and the dielectric constant, and a significant increase in the figure of merit.

4. Doping also increased the hardness of TGS, making it easier to process crystals into infrared detectors.

Other interesting results were obtained from the IML-1 flight experiment, by Dr. James Trolinger at MetroLaser and a graduate student, Mr. J. Sun, at Clarkson University. Spherical plastic particles were suspended in the growth solution. It was expected that these particles would undergo slow movement in response to the residual acceleration in the Shuttle, the so-called "g-jitter." The larger particles were expected to move faster than the smaller ones, with all particles undergoing a random walk more or less in concert. However the results were generally quite different. Nearby particles often moved in different directions at moderately large velocities, with the small particles moving at about the same velocities as the larger ones. We believe this unexpected behavior was caused by vibrations of the cell wall pumping the solution and by high frequency vibrations pushing individual particles.

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FLOATING ZONE MELTING

The primary goal of this project was to produce electronic, optical and detector crystals of greater purity and higher crystallographic perfection utilizing the floating zone melting technique. Crystals under consideration included cadmium telluride, bismuth germanate, bismuth silicate, germanium cadmium arsenide, silver gallium selenide, gallium arsenide, indium antimonide and indium bismuth.

Floating zone melting is a major technique used for crystal growth and purification. A molten zone is formed in a solid rod and caused to move slowly through the rod by moving the rod relative to the heater. Because the melt is not in contact with a container, purity is higher and stress levels are lower than with other solidification techniques. Generation of dislocations, grain boundaries and twins is reduced greatly. There is considerable interest in floating zone melting in space because, for most materials, much larger diameters are possible than can be float zoned on earth. The materials selected for study here covered the full range of properties; both electrical non-conductors and conductors; all constituents non-volatile, one component volatile, and all components volatile; good thermal conductors, moderate thermal conductors, and poor thermal conductors; and both isotropic and highly anisotropic thermal expansion behavior. Thus the results of this program should be invaluable in planning commercial production of any conceivable product by floating zone melting in space.

This project has not yet been completed -- experiments on Spacehab-4 are planned for April 1996 using the ELLI mirror furnace developed by Dornier. (Originally it had been planned to use the Canadian Float Zone Furnace being developed by the Electro-Fuel Corporation for the Canadian Space Agency.) CSA has funded investigators from Dalhousie University and from CANMET. Our CCDS has funded investigators at the University of Florida at Gainesville.

The principal investigator at Florida was Dr. Reza Abbaschian, Professor and Chair of Materials Science. The original plans were to float zone GaAs using liquid encapsulation to avoid arsenic evaporation from the molten zone. Commercial applications for GaAs include high-speed integrated circuits, radiation hard electronics, high-frequency communication devices, light emitting diodes for displays, advanced optoelectronic devices, high-efficiency photovoltaic cells, and infrared optics. These applications are limited by the quality of the bulk semiconductor material from which the devices are fabricated. Higher perfection GaAs was of interest to several of our industrial affiliates, but especially Rockwell.

With its own funds, Rockwell modified its Fluid Experiment Apparatus for proof of concept experiments on InBi on Spacehab 1 in 1993. Four samples, three with different liquid encapsulants and one control sample with argon, were float zoned in microgravity. The growth times ranged from 17 to 35 hours. These CCDS experiments showed that a liquid encapsulant considerably stabilized the molten zone and produced a more cylindrical crystal, especially when the encapsulant was viscous. Stable zones of up to five times the ingot diameter were maintained and translated. Three of the four samples float zoned in microgravity were single crystals.

Recently the project scope was expanded to include liquid encapsulated float zoning of GaSb. This compound semiconductor has potential for advanced commercial electronics applications, including substrates for lasers and IR detectors at long wavelengths, optical communications, and substrates for high signal-to-noise ratio avalanche photodetectors, lasers, and LED's.

With funding from MSAD, Professor Abbaschian also performed a successful flight experiment in 1992 using the French directional solidification apparatus, MEPHISTO.

One early co-investigator at Florida, Dr. Tim Anderson, studied other possible liquid encapsulants for GaAs. Another, Dr. Narayanan, performed computer modeling of convection and heat transfer in the liquid encapsulant and molten zone.

The principal investigators for floating zone melting of bismuth germanate were Drs. David Quon and S.F. Chehab. This work was funded by CSA and was performed primarily at the CANMET labs in Ottawa, beginning in 1992. Note that the stoichiometry, $6Bi_2O_3.1GeO_2$, is not the same as that of "BGO" used commercially for scintillation detectors. Bismuth germanate and its mixtures with the silicate are wide bandgap, high resistivity semiconductors that are photoconductive, acousto-optic, magneto-optic and optically active. Photonics applications include optical information processing, spacial light modulators, photorefractive volume holographic optical elements, and integrated optical devices. Purity and perfection of terrestrially grown crystals are limited and cause problems with applications. Furthermore, attempts to grow mixed crystals of the germanate and the silicate on earth have failed because buoyancy-driven convection has led to large variations in composition. Bell Northern Research, part of Northern Telecom, donated a Malvern Czochralski crystal puller for use in preparing feed crystals.

The principal investigators for floating zone melting of $CdGeAs_2$ were Drs. Vladimir Gelfandbein and David Labrie. This work was funded by CSA and was carried out primarily at Dalhousie University in Halifax. Such ternary compound semiconductors have potential applications in microelectronics and photonics in high-efficiency communication devices, lasers, detectors and integrated circuits. $CdGeAs_2$, for example, has a non-linear optical coefficient 2.6 times that of GaAs, and so is of interest in the photonics industry. Crystals of commercial size cannot be produced on earth. Ampoules cause contamination and breakage (because the thermal expansion is highly anisotropic). Float zoning was completed for the first time under this program, but was only able to produce small diameters because of earth's gravity.

The investigators for CdTe float zoning were Drs. Regel and Wilcox at Clarkson. The commercial applications of CdTe were described earlier. Floating zone melting of CdTe was developed successfully under the direction of Professor Wilcox on a subcontract from the Battelle CCDS. (Float zoning produces higher purity and higher perfection CdTe than directional solidification, but diameters are limited to a few mm because of earth's gravity.)

Computer modeling of float zoning in space was carried out at the Canadian Space Agency by Drs. Ziad Saghir, H-L Chen and Jing Li for bismuth germanate, germanium cadmium arsenide, and liquid encapsulated GaAs. The dependence of the thermal and flow fields on gravity were determined.

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ROBOTIC THERMAL PROCESSING

This was a joint project with NASA Goddard and the SpARC CCDS at the University of Michigan. Our effort was under the direction of Dr. Tim Anderson, Professor and Chair of Chemical Engineering at the University of Florida, and Dr. Eric Cole, Professor of Electrical Engineering at George Mason University. Participating with Professor Anderson was Dr. Kevin Jones, Associate Professor of Materials Science and Engineering at Gainesville. Professors Anderson and Jones were funded through the Consortium via a pass-through grant from NASA Goddard. Professor Cole received his funding directly from Goddard. Mr. Lloyd Purves was the program director at Goddard. The ROMPS GAS Can experiment flew successfully in 1994.

Several companies participated with Professors Anderson, Jones and Cole in the development of experiments to be performed in ROMPS. F.W. Bell helped develop experiments on closed vapor space deposition of InAs Hall generators. The commercial objective was improved noise immunity and repeatability of Hall effect devices. These devices are used commercially for gauss meters, watt meters, limit switches, motor commutation and current monitoring. Applications include controls, elevators and sensors.

Planar Systems planned experiments on rapid thermal annealing of ion implanted and in-situ doped ZnS ACTFEL devices. The commercial objective was enhanced color and reduced power consumption by electroluminescent devices for flat panel displays. Kopin and Spire worked on impurity-induced disordering in GaAs/InP superlattices, for commercial applications in improved optoelectronic devices. Texas Instruments collaborated on solid and liquid phase epitaxial regrowth of Si_xGe_y on silicon for improved high speed transistors for commercial electronic systems and light emitting diodes for commercial displays. Astropower and Photon Energy worked on deposition and solidification of photovoltaic materials for higher performance and lower cost solar cells.

All of the above companies supplied wafers for the flight experiments. Spire, Kopin, TI and Planar Systems performed post flight analysis.

ZEOLITE CRYSTAL GROWTH

The goal of this project was to produce better zeolite catalysts and separation materials. Currently zeolites are popular as catalysts in the petrochemical industry. Higher catalytic yields with greater efficiency would have immense economic benefit. Additional potential commercial applications include oxygen concentrators for high flying aircraft, concentration of waste materials for more convenient storage and disposal, separation and purification of chemicals and gases, and portable kidney dialysis equipment. To realize these benefits requires larger crystals, higher purity, better crystallographic perfection, new structures, and new compositions. Zeolite films would also have applications for hybrid electronic and optical devices.

The zeolite crystal growth project based at Worcester Polytechnic Institute (WPI) was one of the founding Consortium projects. When the Consortium began, Professor Albert Sacco, the PI at WPI, had already prepared a GAS can experiment with university and industry funding. After about two years, the Battelle CCDS became a cosponsor of the WPI project.

The GAS experiment was flown on the Shuttle in 1991. A Shuttle experiment with 38 zeolite solutions was flown in 1992 on USML-1, with Professor Sacco serving as Alternate Payload Specialist. The flight hardware was constructed by Teledyne-Brown Engineering. Three different zeolite phases were grown, at three different temperatures, with four different mixing devices. Significantly larger and more perfect zeolite crystals were obtained in the flight experiments.

In ground based experiments performed in preparation for the two Shuttle missions, WPI discovered additives that significantly increased crystal size and purity. Improved techniques for mixing the solutions were also developed through KC-135 and USML-1 glovebox experiments. Pre-nucleation clustering phenomena were monitored by nuclear magnetic resonance imaging in collaboration with NIST (see following page).

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NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

NIST played a supporting role in the preceding projects. This was one of the founding projects, receiving strong support from all of our corporate members. The principal investigator was Dr. Gabrielle Long, who headed the Materials Microstructure Characterization Group in the Materials Science and Engineering Laboratory of NIST. This group operated two unique X-ray beamports at the National Synchrotron Light Source at Brookhaven National Laboratory, where group members carried out state-of-the-art measurements on ceramic, semiconductor, photonic and other materials of high interest. The group also had an active program involving *in-situ* observation of microstructure development during materials processing by utilizing the NIST slow neutron Research Reactor. Taken together, these programs provided a unique portfolio of advanced materials characterization techniques. Of particular relevance to the Consortium, the group had extensive ongoing research programs involving the imaging of defects in III-V and II-VI single crystals, in man-made diamonds, and in SiC. This team has enabled device manufacturers to produce superior products based on microstructural information not available elsewhere.

NIST also had a contract with MSAD to examine crystals, including those from Consortium members grown under MSAD sponsorship. Comparison was being made between crystals grown on earth and in space.

Dislocation networks and compositional strain fields were observed by x-ray topography in Consortium crystals, including GaAs and CdTe. A Clarkson graduate student, Raghu Balasubramanian, did his doctoral research in collaboration with NIST personnel at Brookhaven. CdTe, GaAs and Si crystals were observed by topography in real time during application of mechanical stress. It was found that dislocations begin to move at a fraction of the engineering critical resolved shear stress.

In another study on CdTe, synchrotron radiation topography and x-ray strain contour mapping were used to compare predictions from the numerical models of Carlson and Moosbrugger at Clarkson with crystals grown by Larson at Grumman using a seeded vertical Bridgman-Stockbarger technique. Good agreement between theory and experiment was obtained. The results indicate that high aspect ratio crystals with controlled orientation and grown with a near-planar freezing interface offer the best prospect for production of large areas of low dislocation density material.

Consortium TGS crystals were also studied. The objective of the TGS investigation was to find the effect of growth parameters on the defect structure and electrical and detector properties. For each TGS crystal studied, two high-resolution x-ray reflection topographs and two high-resolution x-ray transmission topographs were taken. This yielded complete three-dimensional coverage of the TGS microstructure. It was learned that TGS grown on an (001) seed has far fewer defects than TGS grown on an (010) seed. Some dopants caused defects to be introduced, with the lattice strain dependent on the atomic size of the dopant.

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APPENDICES

On the following pages are recent technical reports, the most relevant reprints, and manuscripts submitted for publication.